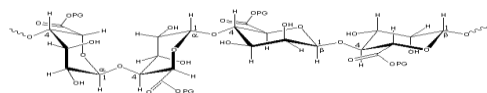




## Functional Materials

# From Inter-crosslinked Bio-hybrid Gels to Carbohydrate Grafted Multilayered Siloxane Nanoparticles

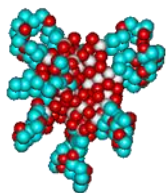
“A journey with nanoparticles and hydrobiogels”



Christophe Bliard



Lu Xu - Andrew Vreugdenhil



CNRS UMR 7312 Institut de Chimie Moléculaire de Reims - URCA - France  
Inorganic Materials Research Lab.- Center Trent University - Canada



E-mail [christophe.bliard@univ-reims.fr](mailto:christophe.bliard@univ-reims.fr)

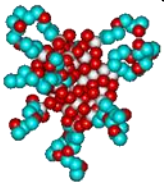




## Plan:

- Nanoparticles:
  - Sol Gel Hybrid Nanoparticules HNP & Bio-Hybrid BHNP modified Carbohydrates & Polysaccharides
    - Réactivity of BHNP
    - Residual BHNP Oxyrane Functionalization
    - Multilayered Bio-Hybrid Nanoparticles MBHN

## -Perspectives





# SiO Nanoparticles by Sol-Gel Techniques

## Sol Gel

Sol-gel process:

Solid gels from metal oxide derivatives SiO, TiO<sub>2</sub>

..

- Low energy
- Aqueous medium, ambient temperature réactions
- Compatible with sensitive biological compounds
- From SiO functionalized nanoparticles
  - Large panel of organic functionalization
- New hybrids inorganic-organic material
- New polysaccharide-Siloxan interpenetrated gels



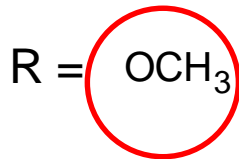
Vreugdenhil et al, *Bio-Inspired Silicon-Based Materials* in « Advances in Silicon Science », vol 5. Springer, 2014



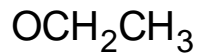


# SiO Nanoparticles by Sol-Gel Techniques

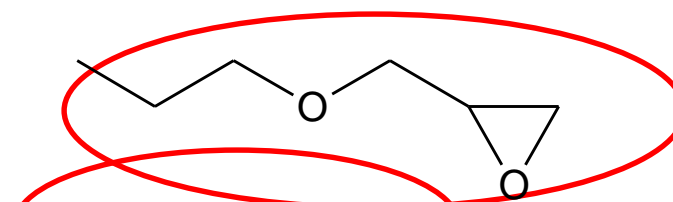
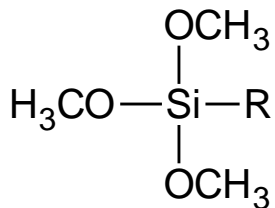
- Silane precursors used to form the sol-gel.
- Possible precursors are:



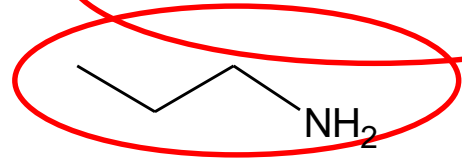
tetramethyloxysilane (TMOS)



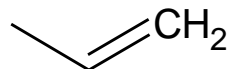
tetraethyloxysilane (TEOS)



glycidoxypropyltrimethoxysilane (GPTMS)



aminopropyltrimethoxysilane (APTMS)



vinyltrimethoxysilane (VTMOS)

Vreugdenhil et al, *Bio-Inspired Silicon-Based Materials* in « Advances in Silicon Science », vol 5. Springer, 2014



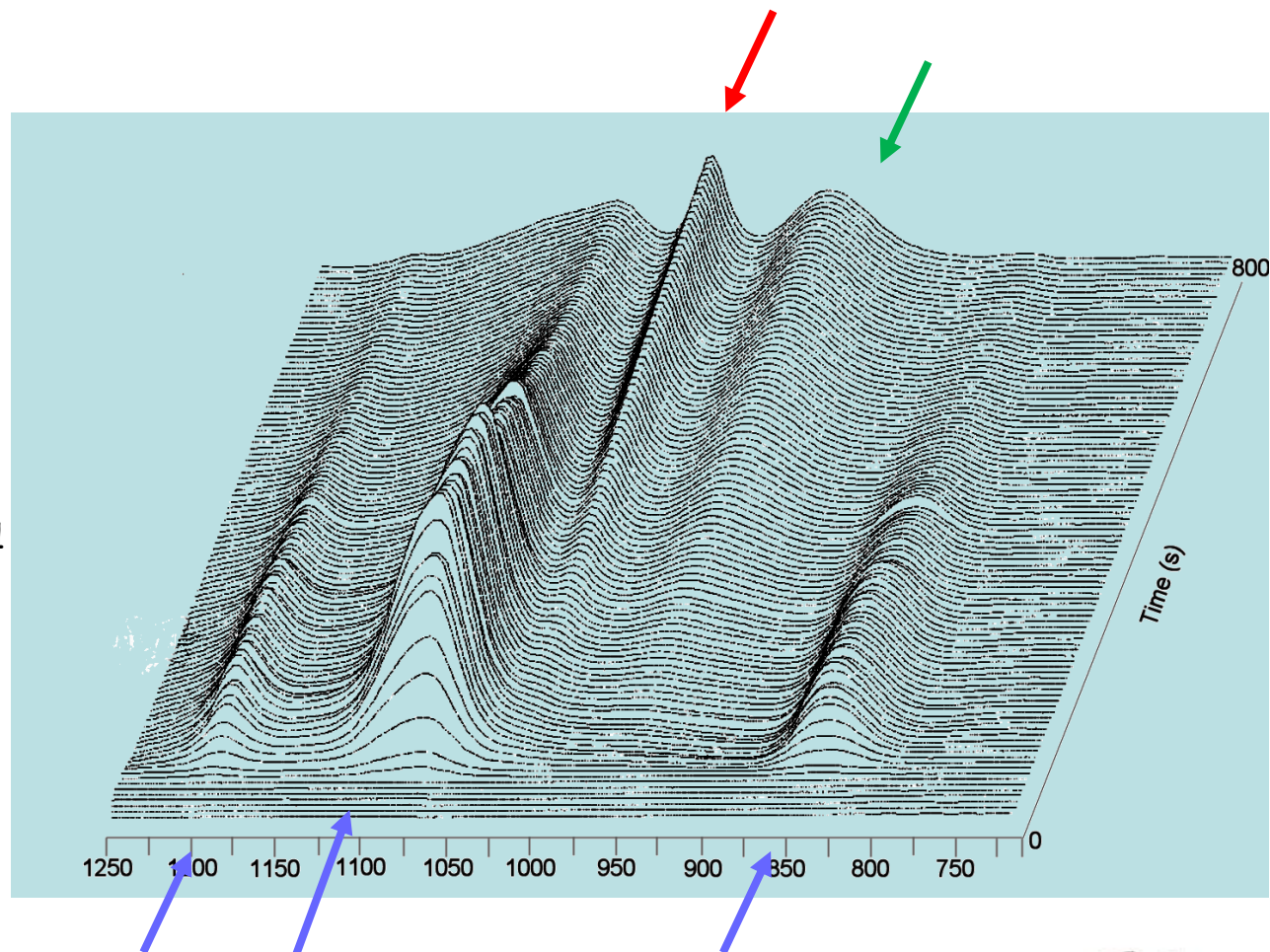






# TMOS: In-Situ IR Analysis

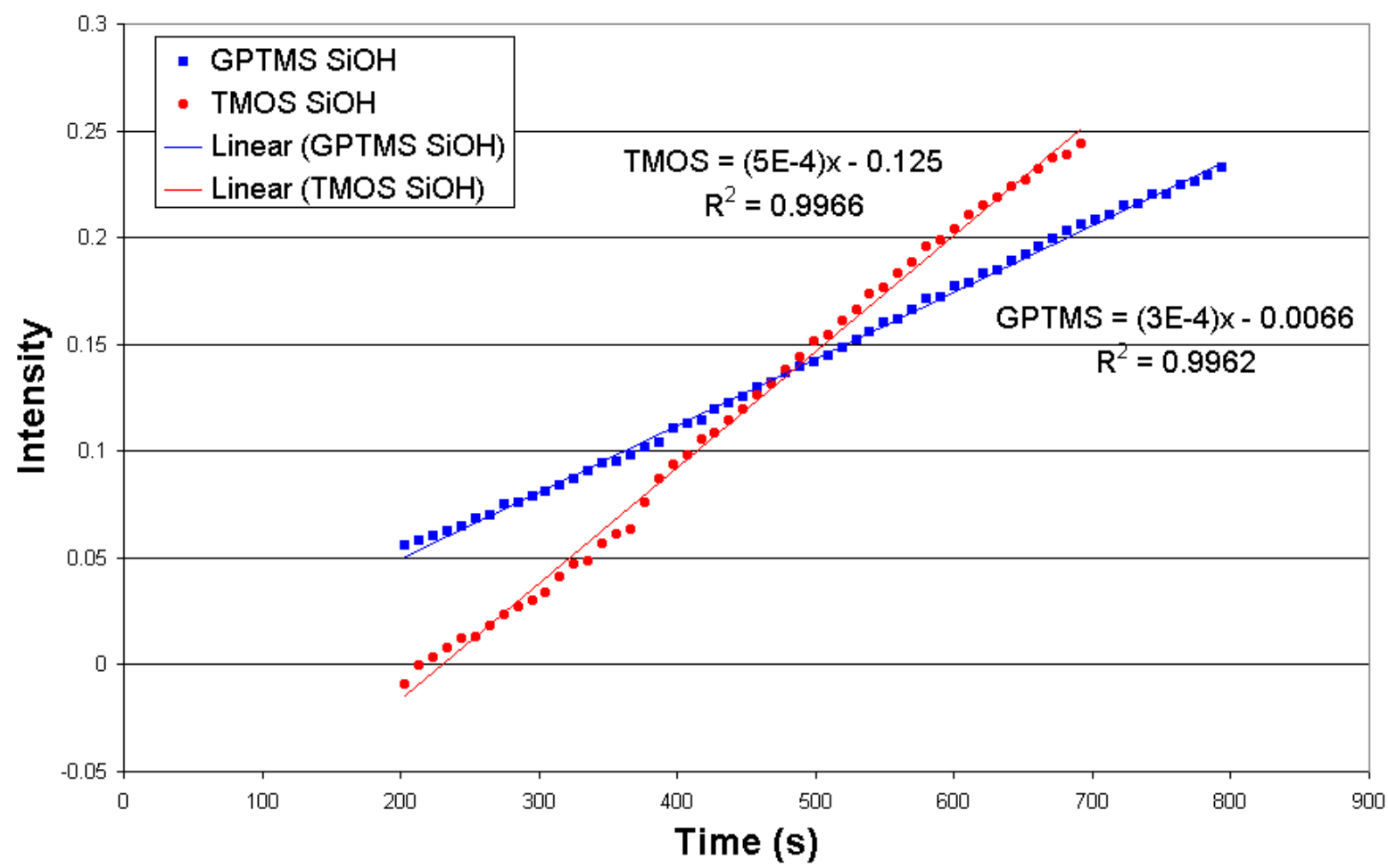
- Methoxysilane precursors
  - $\text{SiOCH}_3$  at 832, 1071, 1196  $\text{cm}^{-1}$
- Hydrolysis products
  - $\text{MeOH}$  at 1018  $\text{cm}^{-1}$
  - $\text{SiOH}$  at 944  $\text{cm}^{-1}$





# Hydrolysis GPTMS vs TMOS

## SiOH Production Rate pH 7

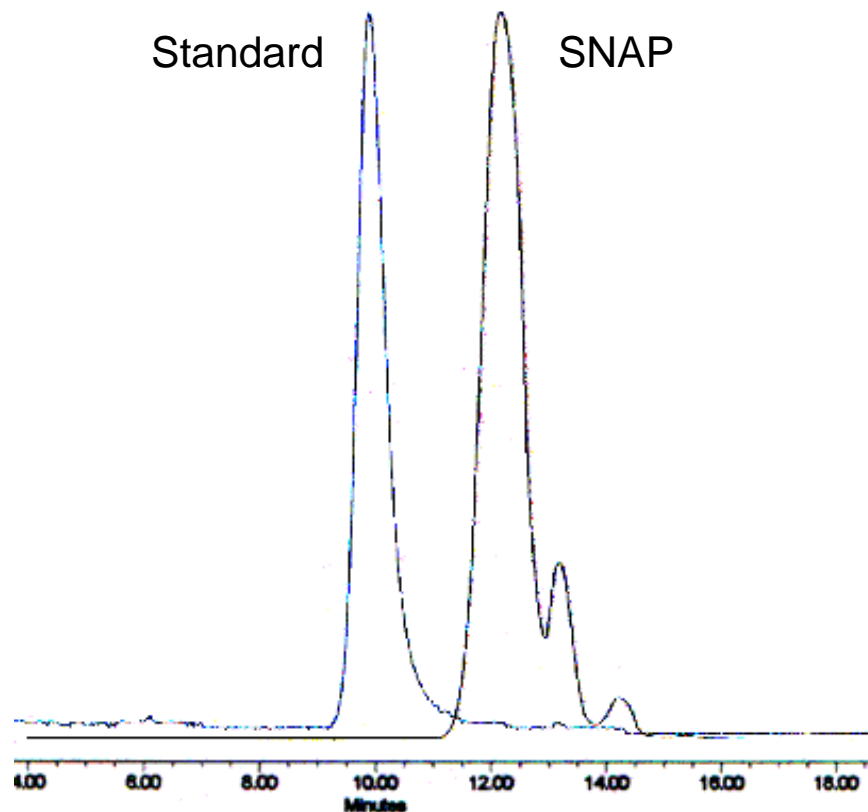


JM



# Particle Size by Gel Permeation Chromatography

- Particles grow in solution ~ 10 K amu
- Reasonable M.wt. distribution
- Correspond to 60-72 silanes per particle
  - 15-18 TMOS
  - 45-54 GPTMS









# Formation of the Bio-Hybrid Inorganic-organic nanoparticles: BHNP

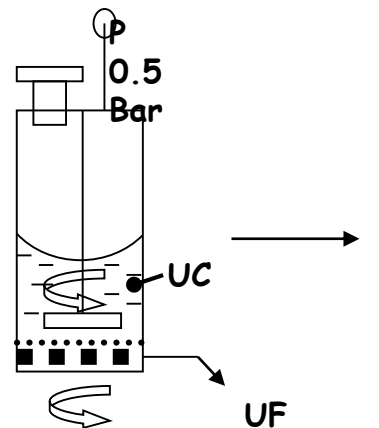


Analyse

## Amino-Acids: (Val, Pro)

### Purification / Ultrafiltration - diafiltration

- Vortex Ultra filtration
- Cellulose Membrane
- MWCO 10 KDa



RMN / D2O  
 Elem. Anal. (N)  
 Polarim. (-)  
 Nanosizer

Diam. (nm)

GT : Dia - (number) 3nm (→ 20 kDa)  
 - (intensity) 8nm (→ 70 kDa)

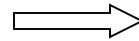
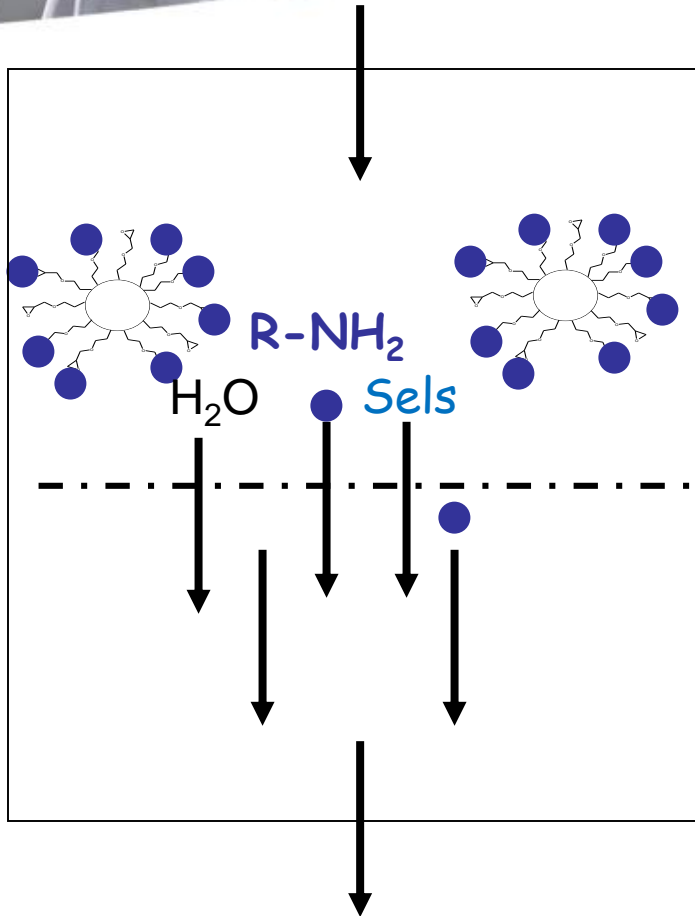
GT  
 Val  
 Pro

8,732  
 26,94  
 61,95

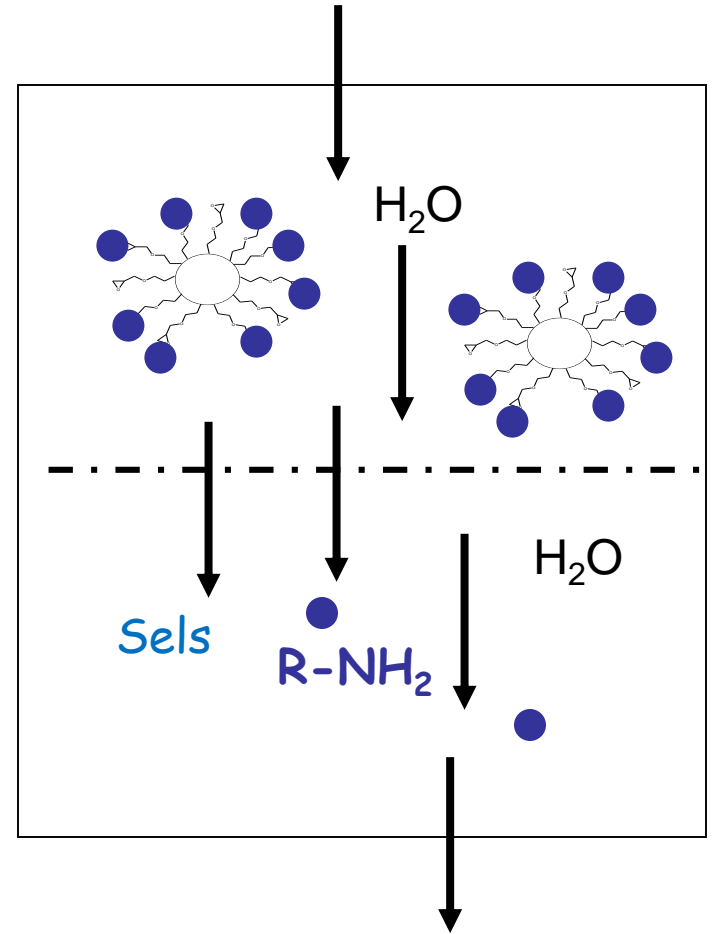




# HNP Purification Ultrafiltration/ Diafiltration



10KDa



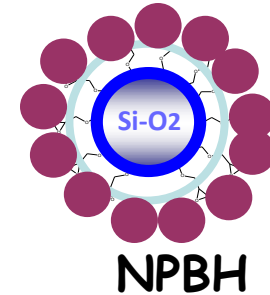
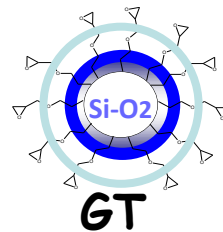


# Formation of Gluco Bio-Hybrides Nanoparticules BHNHP

Sucres

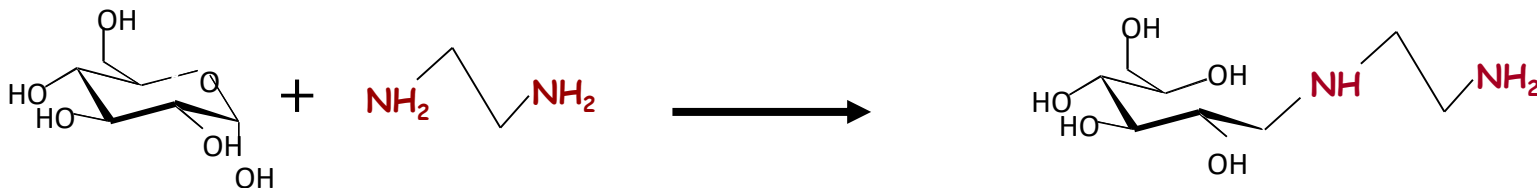
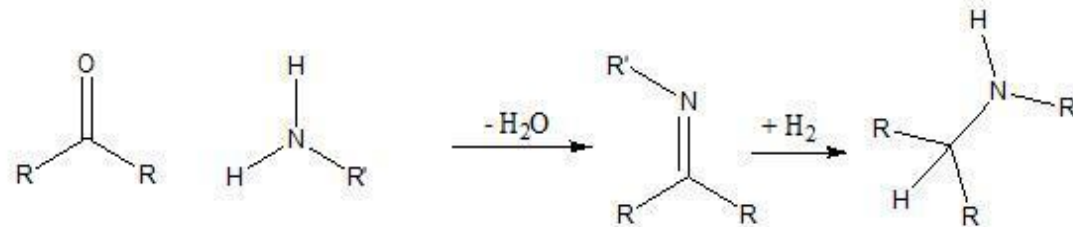
$RNH_2$

+



## Synthesis of $NH_2$ -modified sugar

Reductive Amination  
-  $H_2O$



EA Excess

$NaBH_3CN$

Glucose (Galactose)



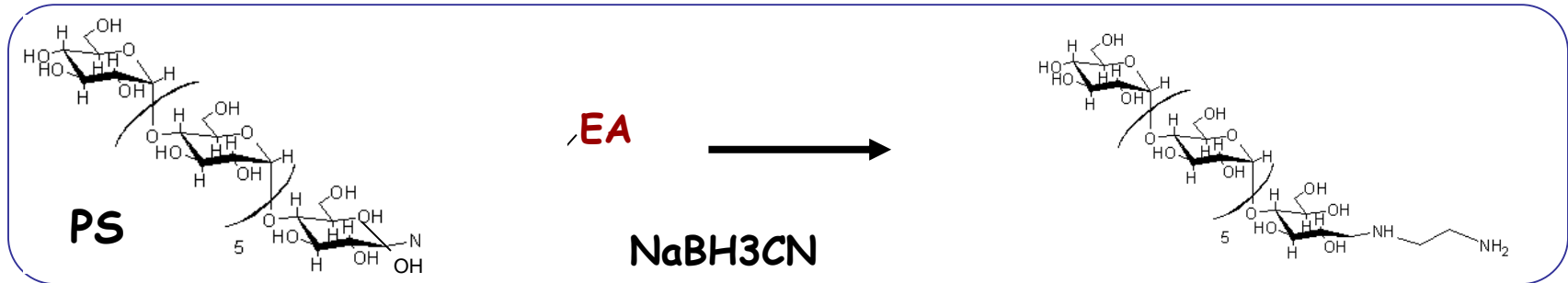
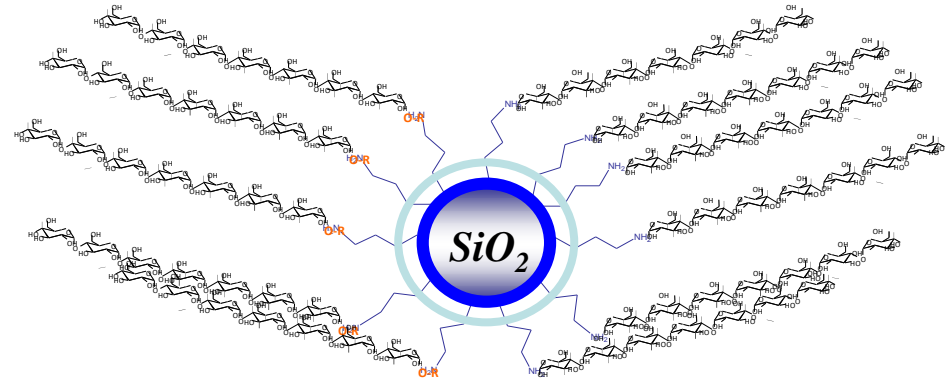
# Formation of Polysaccharide grafted Bio-Hybrides Nanoparticules BHNP



## NH<sub>2</sub> modified Polysaccharides

Noncoating, bioprotection, furtivity...

- Models
- Macro dendrimers
  - hyperbranched polymers
  - rheology.



- Disacch. - Maltose, Lactose, Cellobiose
- Oligo : - Dextrin G-19 (DP7)
- Polysacch. - Lim. Dextrin (DP 40)
- Dextran 10 KDa (DP 50)

- Purif. GPC / UF (CuSO<sub>4</sub>)
- Caract. G19 G19EA EA
- RMN
- MS
- Elem Anal. (N)

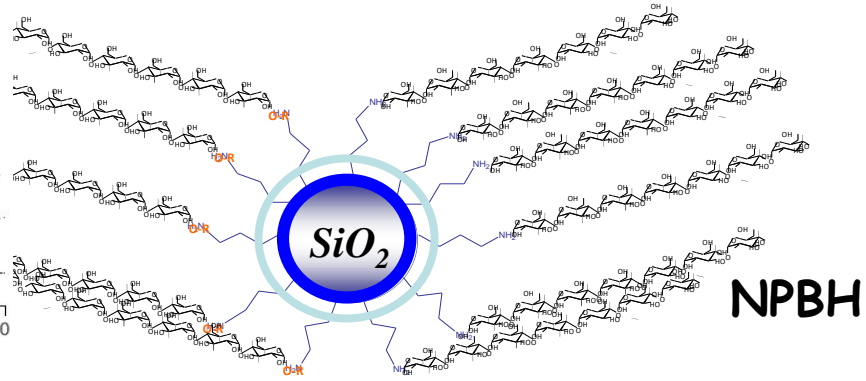
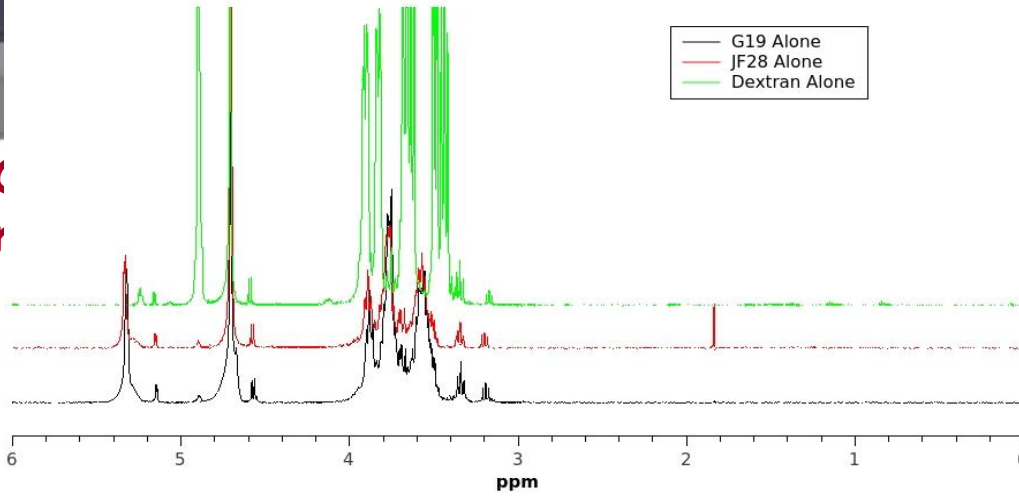




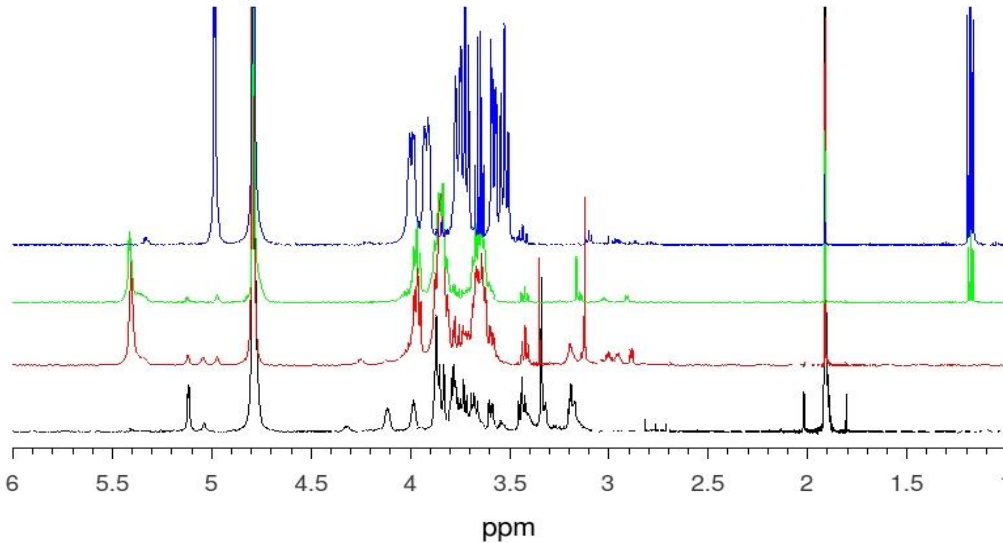


# Formation of Polysaccharide grafted bridges Nanoparticules BHNP

G19 JF28 and Dextran 1H NMR



Polysaccharides EDA Functionalized 1H NMR



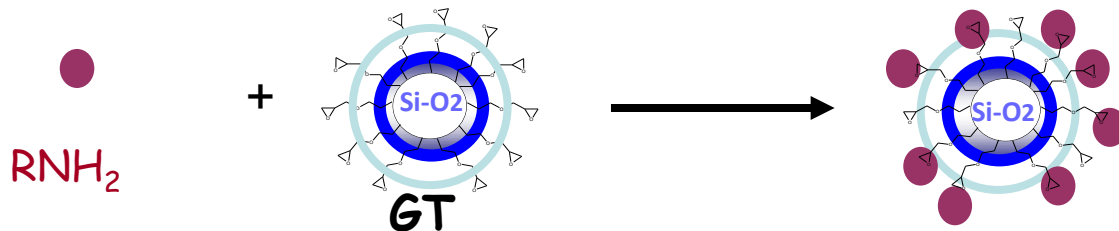
Purif. GPC / UF  
 Charact. RMN  
 Mass Spec.  
 Elem. Anal. (N)

(CuSO<sub>4</sub>)  
 G19 G19EA EA

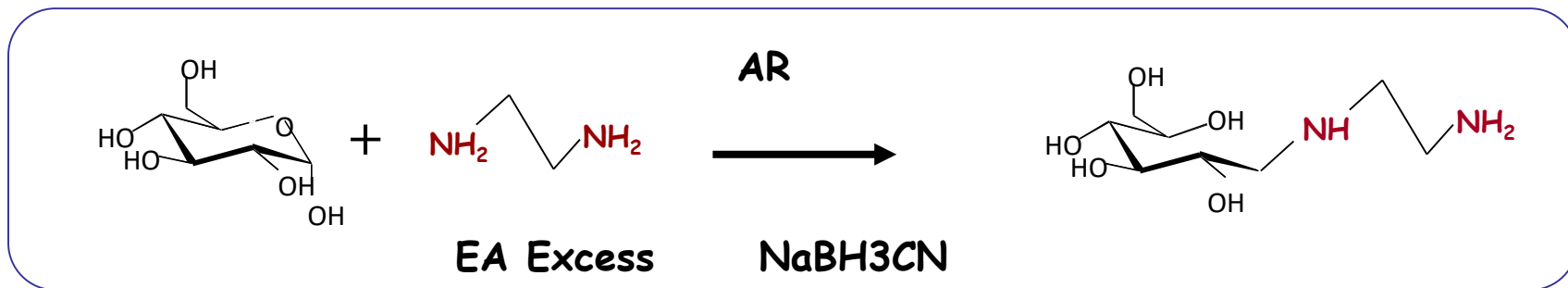




# Reactivity of Glyco Nanoparticules Bio-Hybrides BHNP



## Modified sugars



Glc-EA grafting onto GT  $\rightarrow$  BHNP unstables

NPHB croslinking  $\rightarrow$  gel

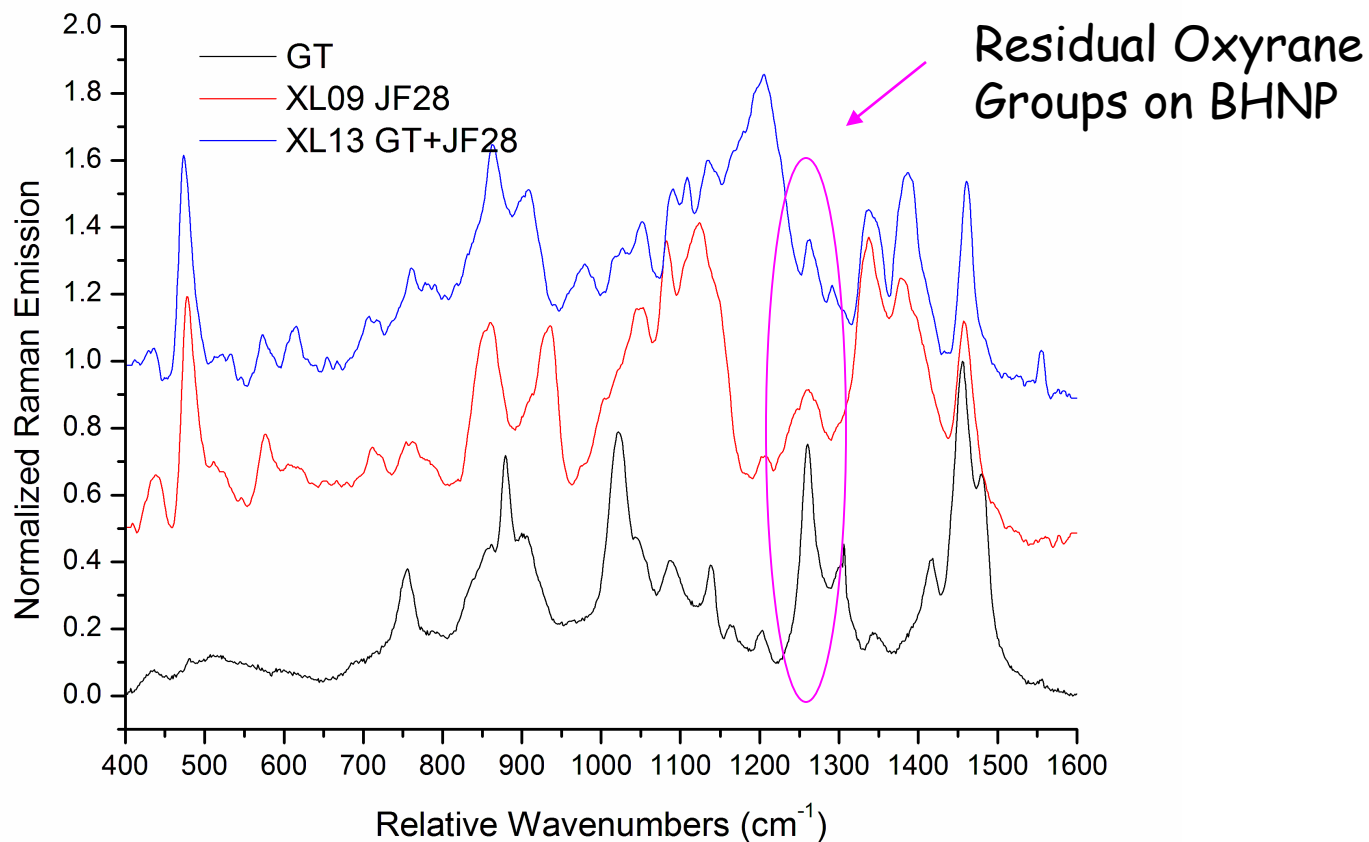
Reactivity of remaining oxyranes groups ?

PS BHNP Stables



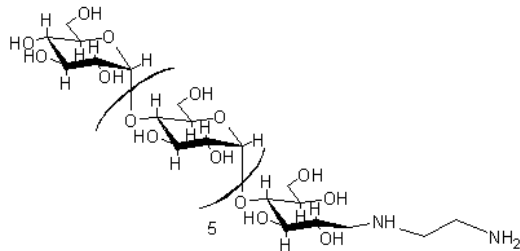
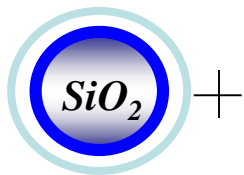


# Characterisation of residual oxyranes on BHNP

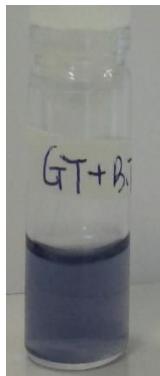
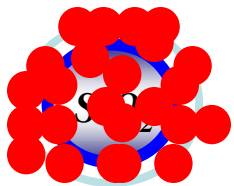
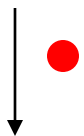




# Secondary Functionalisation of multilayer Bio-Hybrides Glyco Nanoparticules MBHN

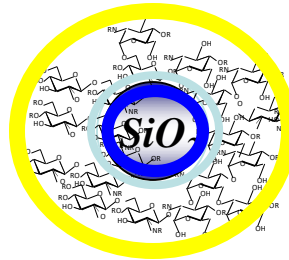
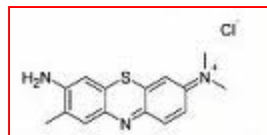


GT

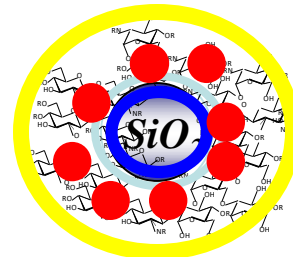


GT ( $11 \cdot 10^{-4}$  Mol/L)

RNH<sub>2</sub>

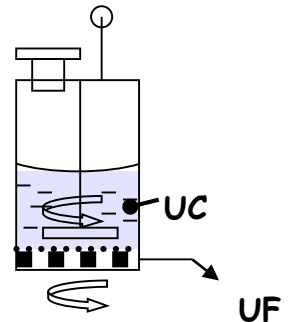


BHNP



MBHN

( $2,2 \cdot 10^{-4}$  Mol/L)





## Perspectives

### Study:

Enzymatic Degradability surface (PS)  
Vectorisation / transport models  
Biological activité  
Furtivity  
Hydrosolubilisation - protection

### Physicochimiques $P^{ties}$ :

Hyperbranched polysaccharide models  
Macro dendrimers  
Rheological  $P^{ties}$   
Primer structure for starch biosynthesis

...







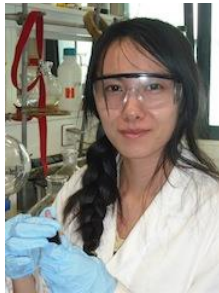
With the precious collaboration of



Maria Carrero Jurado



Andrew Vreugdenhil

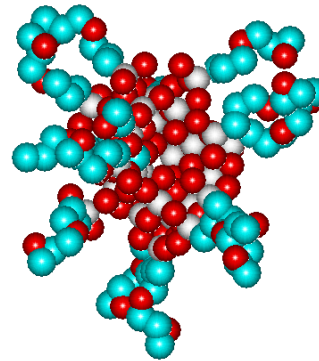


Lu Xu





# Thanks for you attention



Université de Reims Champagne-Ardenne



